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13. ABSTRACT *(Maximum 200 words)*

New methods are explored for producing and characterizing proposed new HEDM molecules – covalent nitrogen and oxygen rings. A laser ablation "supersonic catalytic plasma reactor" was developed, wherein a metal target is vaporized by a pulsed UV laser and reactant gases are added to the buffer gas. A pulsed corona discharge nozzle was developed for the same purpose. Cavity Ringdown and VUV laser ionization mass spectroscopy are Laser Absorption Spectroscopy developed for characterizing the products of the above sources. Initial tests of these sources for producing coinage metal silicides have been carried out.

Cavity Ringdown Laser Absorption Spectroscopy has been extended into the infrared region of the spectrum using two different technologies. Studies of water clusters in pulsed supersonic beams and of molecules in flames have been carried out.

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FINAL TECHNICAL REPORT

AFOSR GRANT #F49620-93-1-0278

"Laser Spectroscopy of Oxygen Rings, Nitrogen Rings, and
Other Novel High Energy Density Forms of Matter"
(Period Covered: 04/15/93-04/14/96)

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During this three year grant period we concentrated on four endeavors related to the central theme of producing and characterizing HEDM species proposed in recent theoretical calculations: 1) Development of a VUV laser ionization scheme for a time-of-flight mass spectrometer, as a diagnostic for the presence of fragile HEDM species (N-rings and O-rings) in supersonic beams. 2) Development of a pulsed supersonic corona discharge source as a means of generating supersonic beams of HEDM species (N-rings and O-rings). 3) Development of a laser vaporization catalytic metal plasma reactor for generating supersonic beams of HEDM species. 4) Characterization of the catalytic plasma reactor system by electronic spectroscopy studies of transition metal silicides, using the cavity ringdown laser absorption spectroscopy (CRLAS) technique developed in connection with this work (7 reprints enclosed). 5) Development of Cavity Ringdown Laser Absorption Spectroscopy in the infrared region of the spectrum for optimum detection and characterization of N-rings, O-rings, and other HEDM species (1 reprint enclosed).

Ph.D. Degree awarded to Dr. James J. Scherer (December, 1994).

Technical Summary

A new class of HEDM molecules has been proposed in a number of recent *ab initio* theoretical calculations. In analogy with known stable cyclic hydrocarbons, covalent oxygen rings (O_4, O_6, O_8, ring ozone), nitrogen rings (N_4, N_6, N_8) and $(NH)_x$ rings (N_6H_6) have been shown to be energetically metastable, although much uncertainty regarding dissociation barriers, excited electronic states, and the corresponding ions remains. The purpose of the research described herein is to attempt the synthesis and characterization of these HEDM molecules in the gas phase. A novel approach has been designed for this purpose, featuring several technical innovations: 1) Catalytic metal plasma expansions were developed for synthesizing and rapidly quenching HEDM molecules. 2) Cavity Ringdown Laser Absorption Spectroscopy was developed to probe the species generated in the supersonic plasma by electronic (and very recently, vibrational) spectroscopy. 3) This was combined with a VUV (118 nm) laser ionization mass spectrometer for detection and characterization of HEDM molecules.

The above systems have been characterized through extensive studies of transition metal silicides (Cu, Ag, Au, and Pt) synthesized by addition of silane to the plasma buffer gas. These were chosen because they involved metals with complimentary catalytic properties and 2) these silicides are very important in electronics materials applications, and were, before this work, very poorly characterized.

Synthesis of HEDM molecules was attempted by the same approach, viz. seeding appropriate precursors into the plasma buffer gas (e.g., N_2 or NH_3 with Pt catalytic metal expansion). Despite a considerable effort, no HEDM molecules have been detailed either by mass spectroscopy or electronic spectroscopy. It is suspected that electronic excitation and/or ionization causes these fragile species to fragment. Accordingly, we have extended the CRLAS spectrometer for operation in the infrared region of the spectrum, such that vibrational transitions of the HEDM species can be monitored. This is likely to be the best approach for detecting these exceedingly fragile molecules.

The Laser Vaporization Plasma Reactor

We have employed the use of a laser vaporization plasma reactor in our attempts to produce HEDM molecules. The central idea behind this approach is to use dense atomic vapors of catalytic metals to atomize chosen precursors to HEDM molecules (e.g., O_2 in the case of O-rings), and to quench the resulting dense atomic vapor very rapidly (microseconds) in a supersonic expansion. This source is a standard Smalley-type laser vaporization source with the one difference being that suitable precursors are seeded in the carrier gas (typically 0.2-2% in helium) and introduced into the source as the target material is being ablated by the vaporization laser. The resulting plasma atomizes the molecules of the precursors, and these atoms then coalesce to form new molecules.

Any highly reactive metastable species formed may then be "frozen out" in local minima in the subsequent collisionless environment of the supersonic expansion. This may be the best way to make HEDM molecules assuming that their production depends on the same type of physical processes that form covalent carbon, silicon, and metal clusters.

Our source (Figure 1) consists of a steel body designed to accept a 0.5 in. target rod, which is continuously rotated and translated using a screw drive. The pulse of gas is supplied from a General Valve Series 9 solenoid valve (0.060 inch orifice), with a backing pressure of 15 - 300 psi. The clustering channel can be removed from the body and interchanged, however the most successful is fan shaped. There are two reasons for this: the first is to allow the vaporization laser, which comes in 22° off normal to the surface of the target rod, access to the rod. This angle is necessary because the first skimmer of a time-of-flight mass spectrometer is located directly in front of the source. The second reason is this geometry increases the interaction length of the supersonic expansion and the probe laser of the direct absorption (CRLAS) spectrometer, resulting in higher sensitivity. The vaporization laser is a 248 nm excimer (Questek 2460) supplying typically 320 mJ/pulse. It is often necessary to attenuate the laser flux by shuttering and/or adjusting the focus onto the target.

We have tested this method of cluster production and compared the results with those obtained using standard laser vaporization for the molecules C_3 and Si_2. Monitoring the 4050 Å C_3 (comet) band, the maximum signal was obtained by seeding 1% CH_4 in helium, and using a backing pressure of 80 psi. By far the best target rod material proved to be either copper or silver, however, C_3 could be generated using a variety of other metals, including gold, niobium, aluminum, and nickel. When carbon was used as the target material, the C_3 signal strength did not change whether or not CH_4 was present in the carrier gas. This implies that the plasma resulting from the vaporization of graphite is in some way insufficient to atomize the CH_4 in the carrier gas. The plasma reactor method was found to produce an order of magnitude more C_3 signal than from laser ablation of a graphite rod (Figure 2). Because we use a direct absorption technique for detection, these results should accurately reflect the relative number density of C_3 in the jet expansion, and therefore show that the plasma reactor method in certain cases is considerably superior to standard laser vaporization.

Similar experiments were also performed utilizing the H-X transition of Si_2. The clusters were formed either by the direct ablation of a silicon rod, or by seeding SiH_4 (~0.2%) in the helium carrier gas and using a catalytic metal plasma. In this case, the direct laser ablation method gave a larger absorption signal, but only by a factor of approximately 1.5.

The ultimate purpose of the plasma reactor, however, was to generate covalent nitrogen and oxygen clusters by adding small quantities of N_2, NH_3, or O_2 to the carrier gas and using platinum

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as the catalytic metal. A more detailed description of these experiments, along with the results are presented in the final section of this report.

The Pulsed Discharge Nozzle (PDN)

Pulsed discharge nozzles have been proven successful in many labs in generating a variety of highly reactive transient species, including free radicals, ions, and clusters.[1] Our PDN source has been employed in much the same manner as the laser vaporization plasma reactor in attempts to produce HEDM molecules. One fundamental difference between these two sources may be the difference in power density of a plasma generated by a laser focused to a small spot on a target rod versus an electric discharge through a high pressure gas. This high pressure glow discharge may be gentle enough compared to laser vaporization to produce the desired cyclic products from suitable precursors.

Our PDN source has been used in two configurations. In the original design, two electrodes are located after a General Valve Series 9 solenoid valve (0.030 inch orifice), separated from each other and the valve by insulators (Figure 3). Our intention for this design was that the discharge occur in the small region between the electrodes during the strongest (highest pressure) part of the gas pulse. To this end, the timing of the gas pulse relative to the high voltage (HV) pulse, the gas pressure and composition, and the interelectrode spacing and distance from the solenoid valve were all varied and optimized by monitoring the signals of products. The channel hole size as well as flare angles for both electrodes could be varied as well. In this manner, we have achieved the same signal to noise ratio for the 4050 Å C_3 (comet) band as with the laser ablation of graphite, by seeding a small amount of CH_4 in helium.

Limitations of the original two electrode design necessitated changing it to incorporate only one electrode. With the two electrode design, we were not able to strike the discharge within the strongest part of the gas pulse, due presumably to quenching processes at higher pressure. In addition, there was evidence of competing discharges to either side of the +HV anode: to the grounded cathode as was intended, but also to the valve body, which was also at ground. Finally, the single electrode design shortened the source length by half, increasing the survival probability of metastable species since they no longer suffer as many destructive collisions within the source before being incorporated in the supersonic expansion.

The timing and duration of the HV pulse is controlled independently of the gas pulse by discharging a charged capacitor which is switched by a fast high voltage, high current transistor (Behlke HTS-81, 8kV pk., 100 nsec). The voltage drop across the plasma region, determined mainly by interelectrode spacing, and gas pressure and composition, is typically 500-1500 volts, with a current of 20-80 mA. The HV pulse is monitored with a Tektronix P6015 probe (40kV pk., 75 MHz bandwidth). Typical HV pulse duration is 30-100 microseconds, currently limited by the

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rise time of the capacitor. After a few hundred microseconds, the discharge becomes unstable due to the rapidly changing pressure profile of the gas pulse delivered by the valve. Typical gas pressure behind the valve is 70-200 psi, seeded with small amounts of N_2, NH_3, or O_2 to the carrier gas. Results obtained with this system are described in a later section of this report.

VUV Photon Generation via Frequency Tripling in Xenon Gas

Possibly an even more difficult problem then making HEDMs in the first place is detecting them once they are made. Mass spectroscopy is by far the most sensitive technique available, but the crucial problem then becomes how to ionize these molecules without destroying them in the process. Single photon ionization is generally a fairly gentle process, however lasers with photons energetic enough to ionize molecules with high ionization potentials in a single step are not generally available. In attempting to find a light source with both a short wavelength and relatively high fluence we have constructed a system to frequency triple a 355 nm. Nd:YAG laser (Continuum NY61-20, 120 mJ/pulse) to obtain 118 nm. (10.49 eV) photons.[2] Essentially, this system is a 10 cm. long tube filled with ~8 torr of Xe gas (Figure 4). Due to the presence of a Xe electronic transition near 118 nm, a third order nonlinear process is greatly enhanced. We have combined this system with a time-of-flight mass spectrometer in our attempts to detect HEDMs.

To test this system we seeded 1% allene (ionization potential 10.03 eV) in helium at a backing pressure of 50 psi. to the General Valve. The single photon ionization molecular beam mass spectrum is shown in Figure 5. The signal to noise for the allene peak is ~1500:1 after 1 min. of signal averaging (~1000 shots), implying a minimum detectable initial concentration for allene of ~10^{14} molecules/cc. This figure will typically vary up to two orders of magnitude for different molecular species as functions of their respective ionization cross-sections. Regardless, the fact that this figure is so large implies a rather poor conversion efficiency into the VUV, contrary to our expectations. Upon conversing with others who have tried this, however, we have found our experience not to be uncommon. The low conversion efficiency of our system is most likely due to the less than perfect beam quality of the pulsed YAG laser. Currently, this technique is less sensitive than the CRLAS spectrometer, which is a rather discouraging result.

Experiments and Results

One set of experiments we have tried involves seeding N_2, NH_3, or O_2 in the carrier gas of the plasma reactor source. We used the mass spectrometer with the 118 nm ionization as the method of detection. Several different catalytic metal target rod materials were tried. Figure 6 shows a mass spectrum taken with 355 nm light as the ionizing wavelength with a copper target rod in a helium buffer containing N_2. The presence of copper nitride clusters shows that free nitrogen atoms are most likely available to form new clusters. Unfortunately, no pure nitrogen or

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oxygen clusters were observed with the 118 nm ionization under any conditions. The main reason for this might be the relatively low sensitivity of this apparatus as a whole due to the low conversion efficiency of the frequency tripling process. It might be possible to remedy this by improving the mode quality of the incoming light and the overall quality of the optical components and alignment of the system. Ultimately, a new laser system may prove necessary for this. Hydrocarbon contamination in the ionization region is another possible reason these experiments were unsuccessful. The cracking patterns of residual hydrocarbons in the ionization region had the same masses as pure N_x or O_x clusters would for C_xH_n, n= 2 to 4. The solution to this could involve more stages of differential pumping using turbo pumps and/or cryopumps to bring the background pressure in the ionization region down from $\sim5*10^{-7}$ torr to 10^{-9} torr. It could also be that the ionization potentials of HEDM candidates lie above 10.49 eV. Atomic and molecular oxygen and nitrogen all have ionization potentials well in excess of 10.49 eV, and it is therefore not unreasonable that metastable molecules formed from these constituents may have higher ionization potentials as well. Unfortunately, no reliable estimates for the ionization potentials of HEDM candidates exists. The PDN was also tried with the VUV mass spectrometer. Again, no nitrogen or oxygen clusters were found, likely due to the problems outlined above.

As stated earlier, our CRLAS spectrometer is actually more sensitive that our 118 nm mass spectrometer. If we had some idea of where the electronic transitions of these HEDMs might lie, and a characterization of the barriers to dissociation in the excited states, attempting to detect them through electronic absorption spectroscopy could be a viable approach. Our spectrometer currently has continuous coverage of the spectral region between 340 nm and 720 nm, and with the addition of a frequency doubler for the dye laser this range could be extended down to 200 nm. However, given the lack of such knowledge, the search problem for HEDMs is incapacitation.

The PDN was also tried in conjunction with an infrared lead salt diode laser spectrometer (Laser Photonics). Because of possible photofragmentation processes upon electronic excitation or ionization, it is likely that detection of HEDM molecules has the best chance for success in the infrared. Unfortunately, O-rings and N-rings are not predicted by high level ab initio methods to have strong infrared intensities. Typical predicted intensities for these molecules are 1-20 km/mole, whereas typical infrared intensities for pure carbon clusters routinely detected in our laboratory with the diode laser spectrometer are many orders of magnitude higher ($C_9 \sim 40,000$ km/mole).

Perhaps a more serious obstacle in detecting HEDMs with the infrared diode laser spectrometer and the PDN source is lack of required sensitivity, due to a number of factors. The diode laser spectrometer is noisy, due mostly to the vibrations inflicted on the diode from the piston of the closed-cycle refrigerator unit's cold head, although this is by far not the only source of noise. Without an adequate filtering scheme to remove these low frequency vibrations, the

sensitivy is very poor, typically only roughly a few parts in 10^3 (e.g. we often have experienced roughly 70 mV rms of noise on a 20 V baseline from the detector's preamplifier, which corresponds to 0.0035 of the ~400 microwatts of the available laser power available for detection of HEDMs). Laser vaporization methods, including pure carbon cluster formation from excimer ablation of graphite rods, effectively allow filtering of much of the diode laser noise and detector noise while maintaining most of the signal amplitude by sending the detector output through a 10 kHz high-pass filter and a 20 kHz low-pass filter. These filters ac-couple the absorption signals, giving them both positive and negative voltage components spaced about 20 microseconds apart, which can be sampled with two boxcar averagers. When the laser is off resonance, these two boxcars subtract background fluctuations. Most of the signal amplitude is maintained through this filtering system because of the ultra-short time profile of the signal, which is dependent on the pulse width of the excimer laser, 15 nanoseconds. The ultimate sensitivity of this method has been determined to be a few parts in 10^5.

On the other hand, the time profile of the PDN is order of magnitudes longer, 30 to hundreds of microseconds, meaning that the corresponding frequency bandwidth is much narrower than for laser vaporization. Since the signal would then have far fewer components in the high frequency bandpass where much of the noise is filtered out, much of the signal amplitude would be lost as well. Efforts to detect c_{2v} ozone (a probable precursor to the cyclic-ozone HEDM and thus a good "practice" molecule for optimizing the PDN and diode laser spectrometer), the C_2H radical, and pure carbon clusters, C_3, C_6, and C_9 with available diodes have all failed. Many filtering schemes were tried to extract signal, including the use of gated lock-in techniques employing boxcar averaging the output of a lock-in amplifier. The difficulty here is that the time profile of the PDN signal falls midway between the ultra-short time regime, where the use of bandpass filtering with boxcar detection is optimal, and dc signals, which work best with lock-in assisted detection.

Use of the laser vaporization plasma reactor in connection with the diode laser spectrometer then seems to be the next logical step; the filtering scheme enjoyed by the carbon cluster experiement would apply here as well. Unfortunately, we are also plagued by a tedious search problem in these ultra-high resolution experiments.

Further modifications to the PDN may help. A slit version of the single electrode design may be inexpensively built which would increase sensitivity relative to the current pin-hole version by increasing the effective interaction length of the probe laser with the absorbing species in the resulting planar supersonic expansion, and by minimizing Doppler broadening. Slit sources have been constructed in our laboratory for the formation of weakly-bound water clusters, amino acid containing clusters, clusters containing ions and free radicals, and metal clusters, with promising results.

Infrared Cavity Ringdown Laser Absorption Spectroscopy: A Powerful New Probe for Unstable Species

We have recently succeeded in extending the CRLAS method into the infrared using two different technologies. At Berkeley (Figure 7), we downconvert our existing tunable dye laser into the IR by Stimulated Raman Scattering (SRS) in either a cesium heat pipe or in a high pressure cell. This produces broad spectral coverage with usable power levels, but the spectral resolution is limited, which limits both the sensitivity of the CRLAS method and the information that can be extracted from spectroscopic studies. Nevertheless, we have succeeded in detecting clusters in jets and molecules in flames with this approach. In Figure 8 we show vibrational spectra of water clusters obtained by IR-CRLAS. As long as the linewidths of the molecular transitions are sufficiently large relative to the 0.5 cm^{-1} laser bandwidth, then the method has high sensitivity. Unfortunately, this is not the case for either the catalytic plasma expansion or the pulsed discharge nozzle, and we cannot address these systems without achieving a higher level of spectral resolution, e.g., as available from a modern optical parametric oscillator (OPO) system.

We have collaborated with the Rakestraw group at the Sandia Combustion Facility in Livermore to test the IR-CRLAS approach with state of the art transform-limited pulsed IR lasers. They operate an OPO/OPA system which produces 3.5 ns pulses with bandwidths of .0035 cm^{-1} and pulse energies exceeding 1 mJ at 10 Hz over the range 1.3 - 4.5 μm (Figure 9). This system is nearly ideal for IR-CRLAS experiments. We have found an absorption sensitivity of 2×10^{-6} at 1.6 μm and 4×10^{-4} at 3.3 μm, where the best available mirrors (R=99.2%) limited performance representative spectra taken with this system are shown in Figure 10. It is clear that the combination of CRLAS using a state of the art infrared laser system with our supersonic plasma reactor and pulsed discharge nozzle would present a large number of exciting new possibilities, including the best chance at detecting and characterizing HEDM molecules.

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Figure Captions

Figure 1.   **Laser vaporization plasma reactor.** A dense atomic plasma, created by ablating a metal target with a vaporization laser, atomizes chosen precursors to HEDM molecules entrained in a carrier gas (0.2-2% in helium). The resulting atomic vapors are then quenched very rapidly in a supersonic expansion, which they may then coalesce to form new molecules.

Figure 2.   **C_3 produced in a catalytic plasma versus laser vaporization.** The upper trace corresponds to C_3 generated by flowing CH_4 seeded in helium over a silver target rod. The bottom trace is from laser vaporization of a graphite rod.

Figure 3.   **Pulsed discharge nozzle source.** An intense discharge pulse in the small region between two electrodes in the exit channel is timed to occur within the strongest (highest pressure) part of a gas pulse. This high pressure glow discharge may be gentle enough relative to laser vaporization to produce the desired cyclic products from suitable precursors.

Figure 4.   **VUV photon generation by frequency tripling in rare gases.** Single photon ionization of metastable HEDM molecules will allow the use of extremely sensitive mass spectroscopy techniques for their detection. The presence of an electronic transition near 118 nm in xenon greatly enhances the third order nonlinear generation of 10.49 eV photons from the frequency tripling of the third harmonic of a Nd:YAG laser at 355 nm.

Figure 5.   **VUV single photon ionization of allene in a molecular beam.** 1% allene (ionization potential 10.03 eV) was seeded in helium at a backing pressure of 50 psi. The peak marked with an asterisk is due to an impurity in the allene source, while the others are due to hydrocarbon contamination in the ionization region.

Figure 6.   **Copper nitrides produced in a catalytic metal expansion.** This time-of-flight mass spectrum of copper and copper nitride clusters using 355 nm (multi-photon) ionization was taken using a copper target rod in a helium buffer containing N_2. The presence of copper nitride clusters implies that free nitrogen atoms are available to form new clusters.
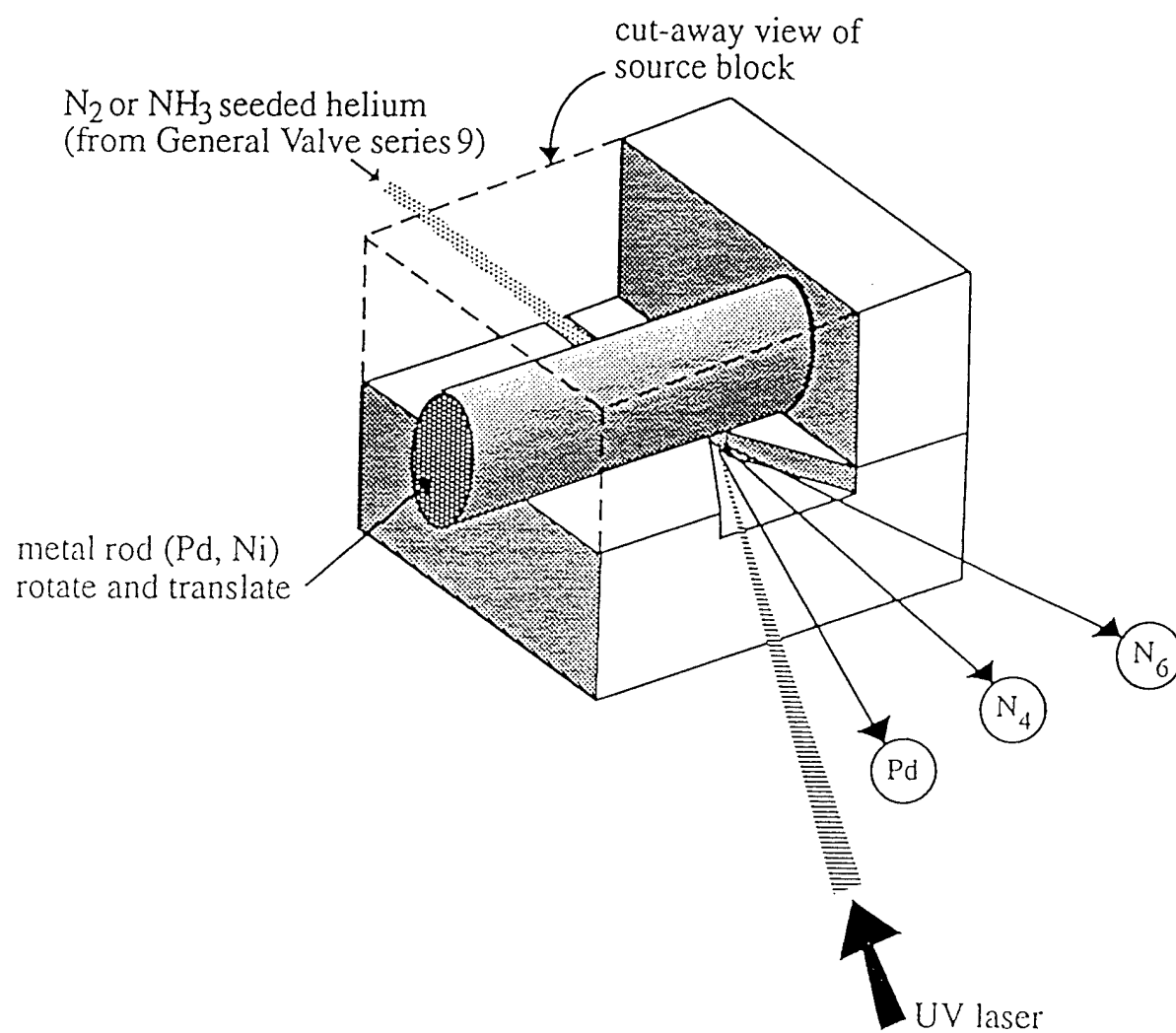
Figure 7.   **The Berkeley IR-CRLAS apparatus.** We downconvert a tunable dye laser into the IR using Stimulated Raman Scattering (SRS) in a cesium heatpipe. This produces broad spectral coverage, but the spectral resolution is currently limited to 0.5 cm^{-1} (15 GHz), due to processes inherent to SRS.

Figure 8.   **IR-CRLAS spectra of water clusters produced in a pulsed supersonic beam.**

Figure 9.   **The Sandia IR-CRLAS apparatus.** Single mode pulsed infrared laser light (0.0035 cm^{-1}) is generated in an optical parametric oscillator (OPO) and coupled into the ringdown cavity with a simple telescope.

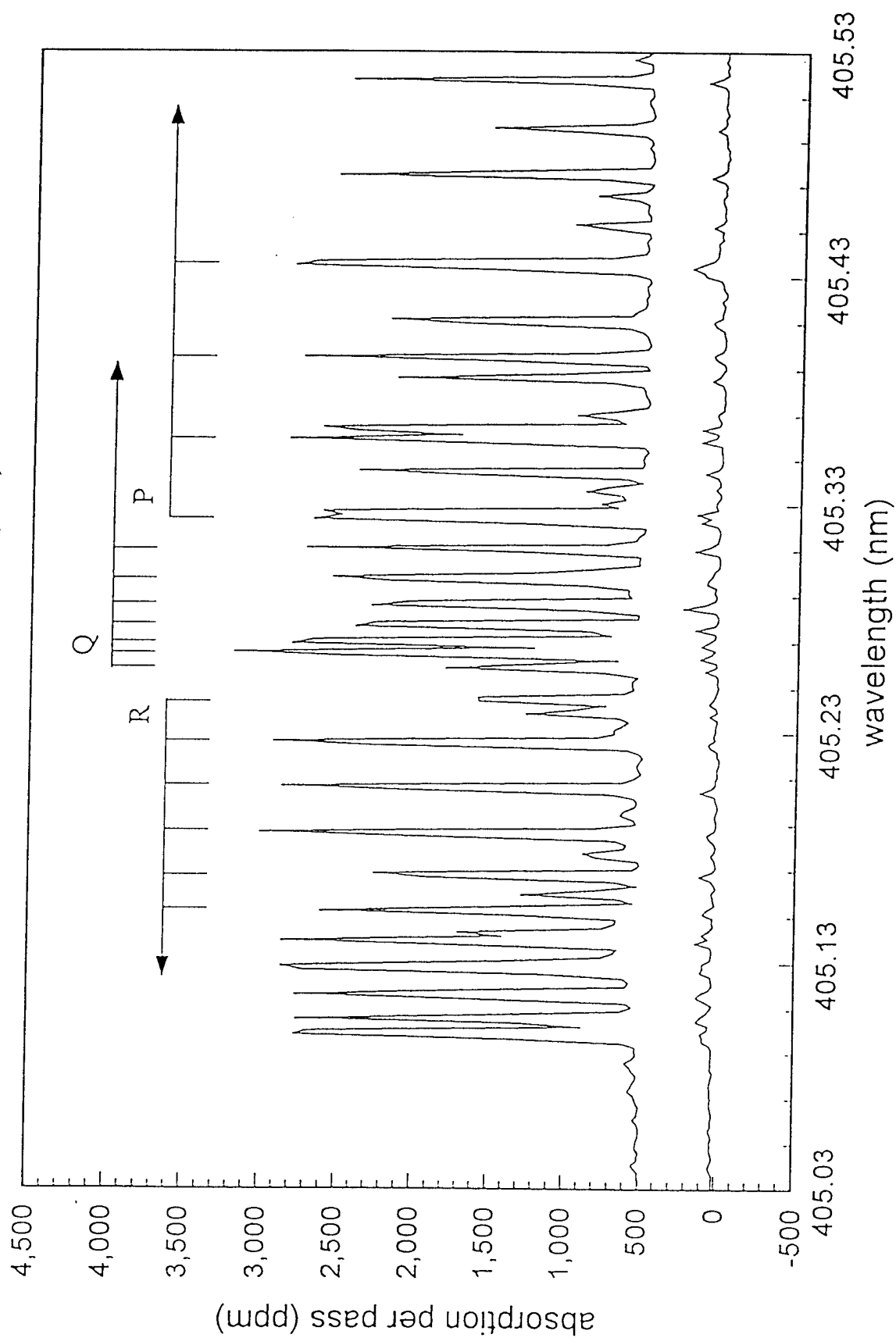Figure 10.   **IR-CRLAS spectra of the Q-branch region of the ν_3 fundamental of CH$_4$.**

Figure 1

Catalytic Plasmas

cut-away view of source block

N_2 or NH_3 seeded helium (from General Valve series 9)

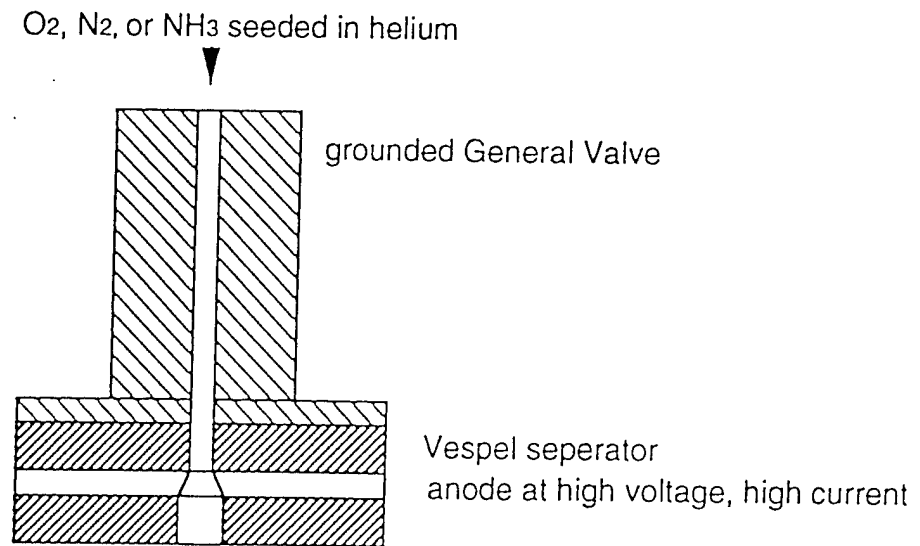metal rod (Pd, Ni) rotate and translate

N_6

N_4

Pd

UV laser

- Vary timing between laser and gas pulses
- Vary laser fluence: hot dense plasma to gentle photolysis

Figure 2

C$_3$ A$^1\Sigma$ - X$^1\Pi$ (0,0)

Figure 3

Pulsed Discharge Nozzle (PDN)

O2, N2, or NH3 seeded in helium

grounded General Valve

Vespel seperator
anode at high voltage, high current

-Vary timing, power of HV pulse independent of gas pulse

- Vary interelectrode spacing, nozzle geometry

- Voltage drop typically 500-1500 V, current 20-80 mA

- Typical pulse duration 30 to 100 microseconds
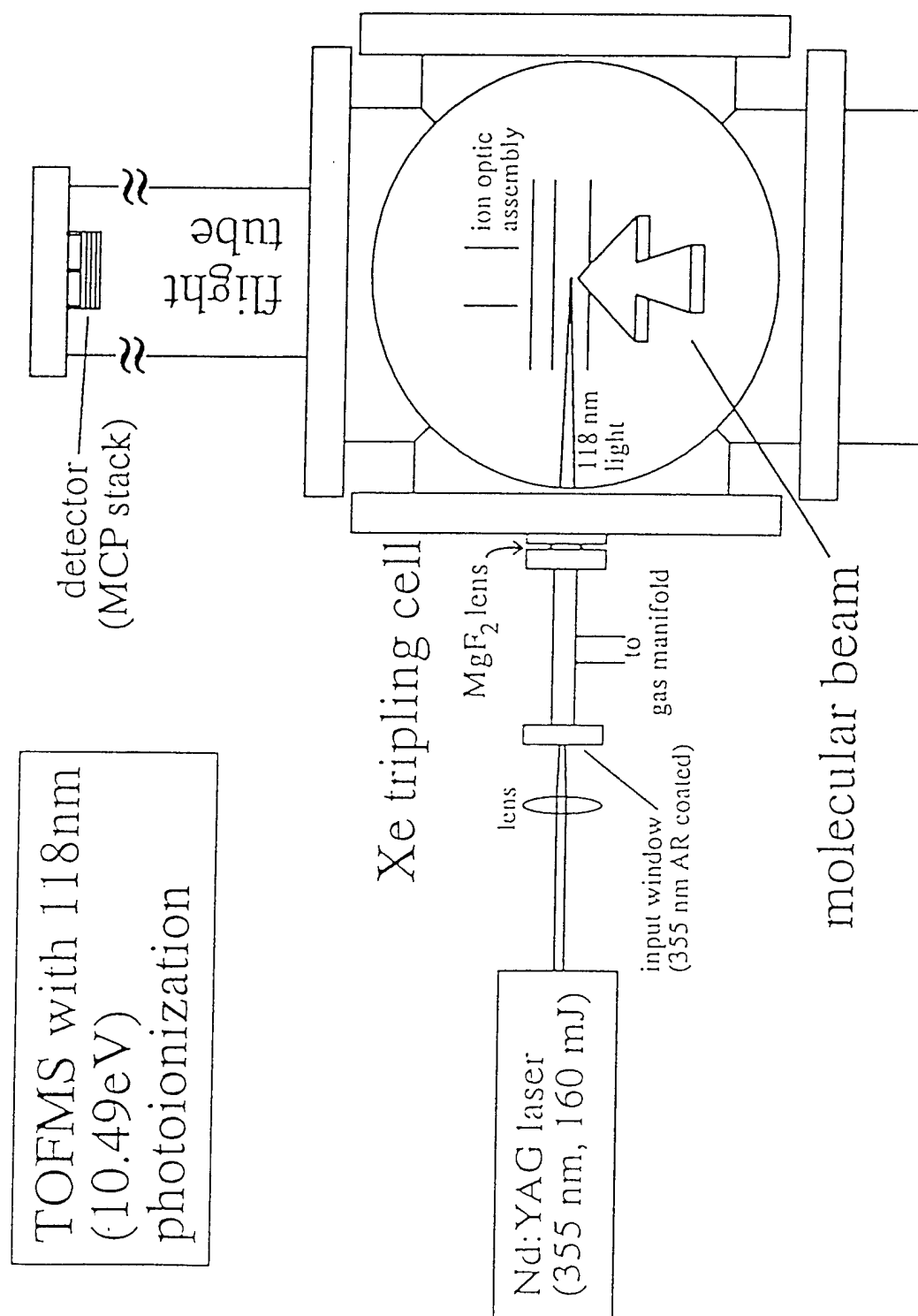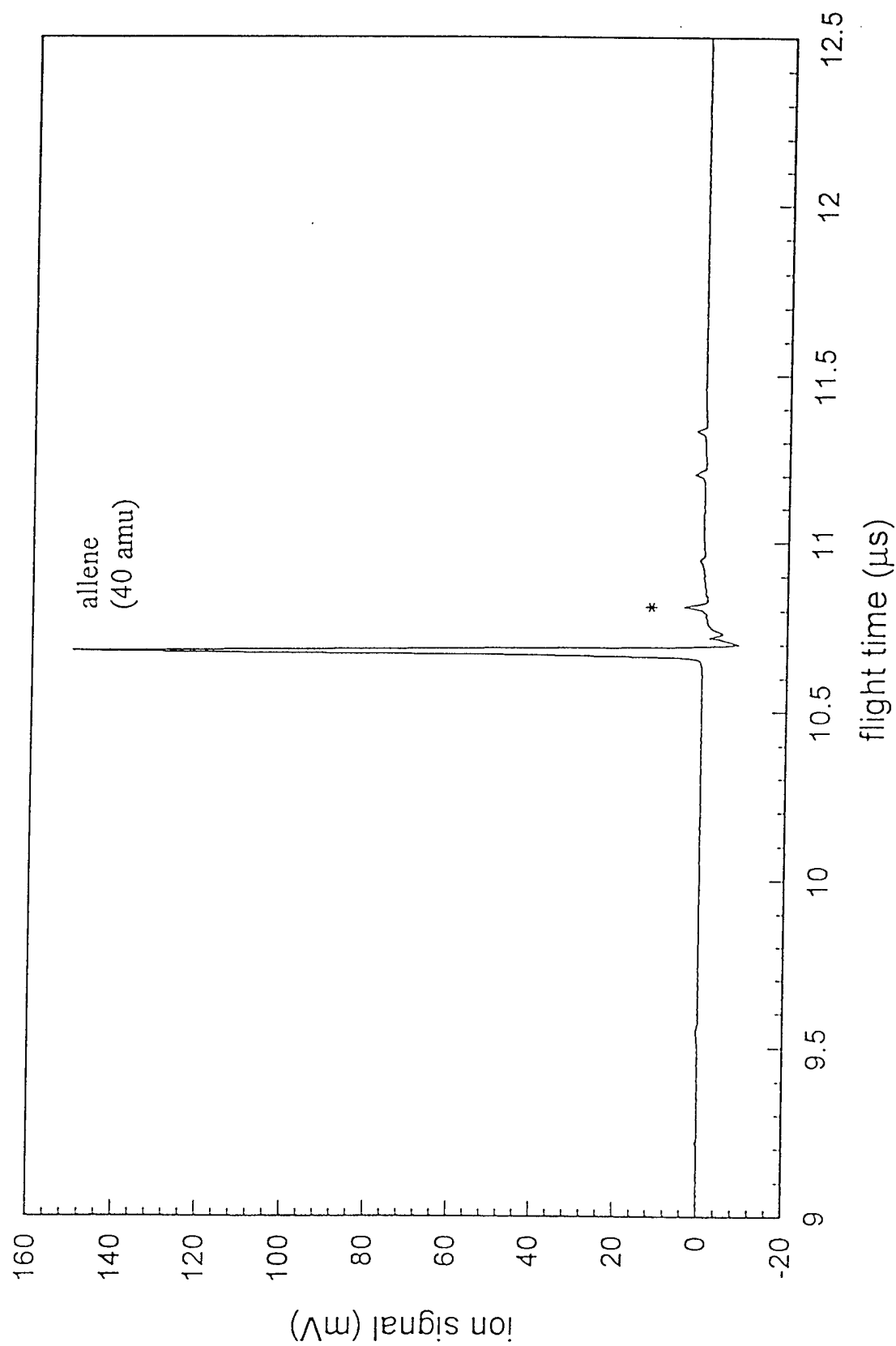
figure 3

Figure 4

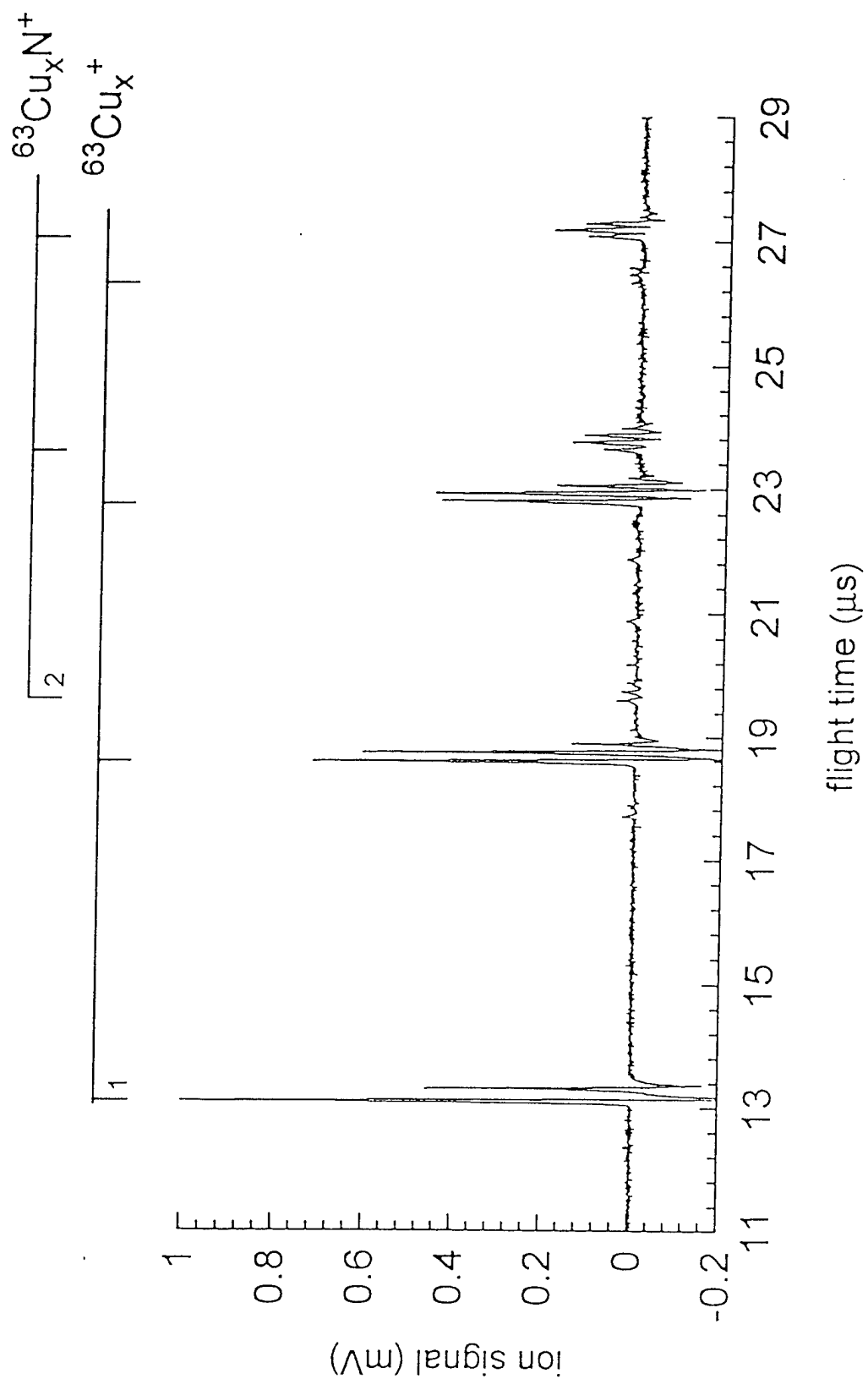TOFMS with 118nm (10.49eV) photoionization

Xe tripling cell

detector (MCP stack)

flight tube

ion optic assembly

118 nm light

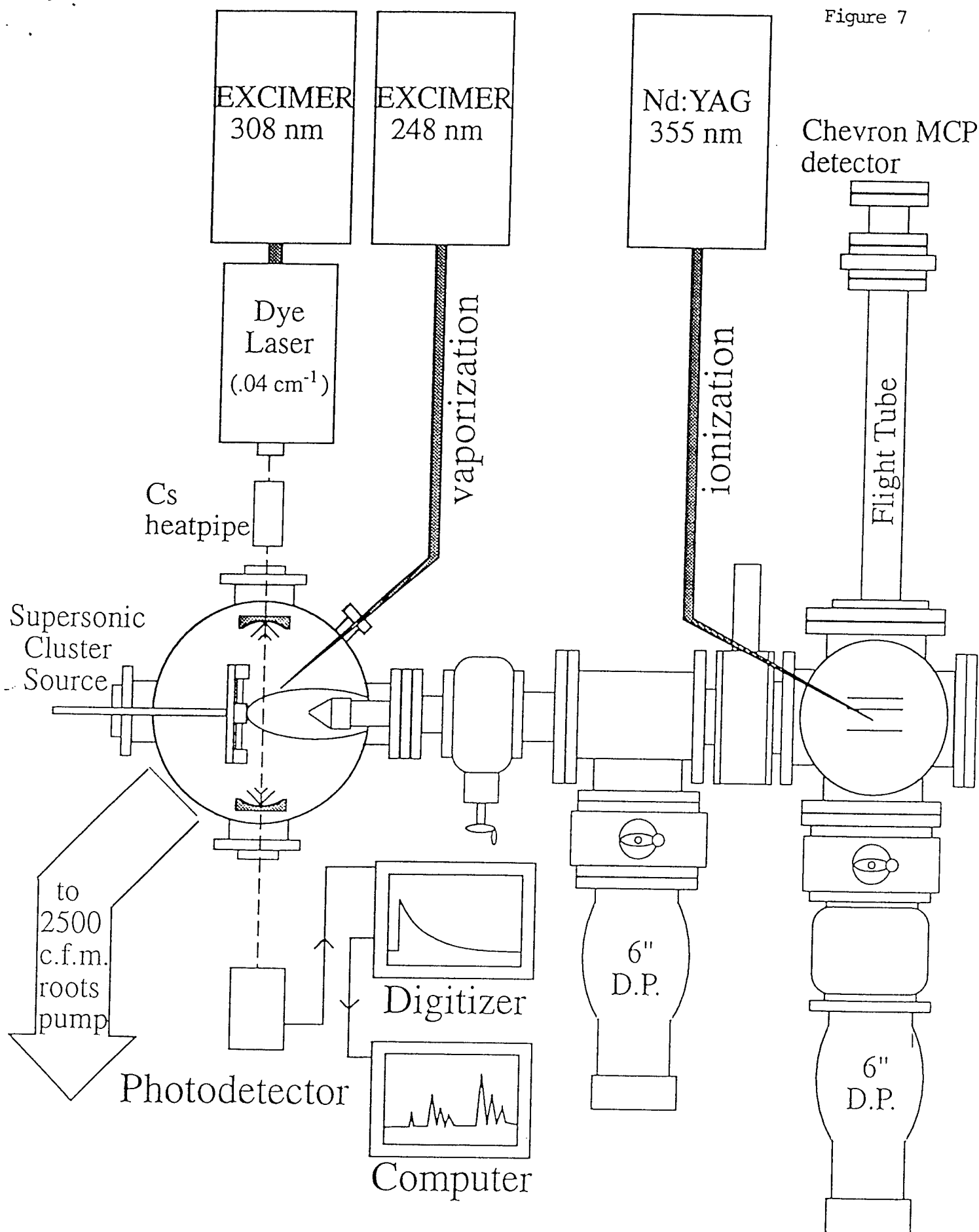MgF$_2$ lens

to gas manifold

lens

input window (355 nm AR coated)

Nd:YAG laser (355 nm, 160 mJ)

molecular beam

Figure 5

Figure 6

Figure 7

EXCIMER
308 nm

EXCIMER
248 nm

Nd:YAG
355 nm

Chevron MCP
detector

Dye
Laser
(.04 cm^{-1})

vaporization

ionization

Flight Tube

Cs
heatpipe

Supersonic
Cluster
Source

to
2500
c.f.m.
roots
pump

Photodetector

Digitizer

Computer

6"
D.P.

6"
D.P.

Figure 8

free O-H region

dimer

trimer

tetramer

pentamer

frequency (cm^{-1})

3600

3400

3200

3000

400

300

200

100

0

absorption per pass (ppm)

Figure 9

Figure 10

Figure 10